THERMAL ANALYSIS OF THE COAL-ZINC CHLORIDE SYSTEM

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INTRODUCTION

Zinc chloride is known to be an effective catalyst for coal hydrogenation and for hydrocracking coal extracts. Weller et al[1] studied the batch hydrogenation of coal and found that zinc showed appreciable catalytic activity in the presence of ammonium chloride. They also found that zinc could replace up to 90% of the tin in a tin-ammonium chloride catalyst without appreciable loss of catalytic activity. Zielke et al[2,3] have studied the hydrocracking of coal, coal extracts and polynuclear hydrocarbons by molten salt catalysts. They found zinc chloride to be an effective hydrocracking catalyst for polynuclear hydrocarbons, but inactive for the hydrogenation or hydrocracking of single-ring aromatic molecules. Stannous Chloride was relatively inactive for hydrocracking although it is a good hydrogenation catalyst for coal. Zinc chloride and stannous chloride are both found to be good catalysts for the hydrogenation of coal in a short-residence-time reactor.[4] This study of the coal-zinc chloride system was initiated because of the potential use of zinc chloride as a catalyst for the large-scale hydrogenation of coal. The present investigation covers the thermal behavior of the coal-zinc chloride system in the absence of hydrogen.

EXPERIMENTAL

Hiawatha, Utah coal was used in these experiments. This is a high volatile bituminous coal of 47% volatile matter (dry, ash free basis). The particle size was -60 + 100 mesh.

MCB reagent grade zinc chloride was impregnated on the coal from aqueous solution. The coal was mixed with just enough solution to thoroughly wet the coal and the mixture was dried for two hours at 100°C in a vacuum desiccater. This was found to give a uniform distribution of the zinc chloride.

Thermogravimetric analysis was performed on a Fisher TGA System. A Cahn model RG microbalance was used to measure weight changes. A Fisher model 360 temperature programmer was used to control the temperature. The temperature was programmed at a linear rate from 105 to 900°C. Nitrogen gas flowed over the sample at a rate of 0.2 l/min. Approximately ten milligrams of sample were used in these experiments. Weight losses are corrected for the effect of nitrogen gas flow and for a non-volatile residue in the zinc chloride.

Pyrolysis products were analyzed on a Packard model 7401 gas chromatograph. An eight foot column of activated alumina was used for separation and a flame ionization detector was employed.

RESULTS AND DISCUSSION

The integral and differential weight losses of a sample of Hiawatha coal are shown in Figure 1. The curves are corrected for moisture, but not for the ash content of the coal. The heating rate is 10°C/min. As zinc chloride is impregnated on the coal, the thermograms are altered. The weight loss below 400°C increases due to the loss of zinc chloride. The maximum in the differential weight loss curve is lowered and the loss of weight by the coal is significantly reduced. Table I shows the effect of increasing amounts of zinc chloride. The effect of the heating rate is also shown. The heating rate has little effect on the weight loss of pure coal, but increasing heating rates increase the weight loss of coal impreg-

TABLE I
Thermogravimetric Analysis of Coal-Zinc Chloride

Heating Rate, °C/Min.	Weight % $ZnCl_2$	% Weight Loss of Coal at 900°C
5	0	40.4
5	2	36.9
5	5	33.5
5	8	30.6
5	12	28.6
5	15	26.5
5	20	25.4
5	25	25.2
10	0	40.1
20	0	40.7
10	12	29.5
20	12	30.1
5	5 (Physical Mixture)	33.1
5	12 (Physical Mixture)	29.7
5	20 (Physical Mixture)	28.1
5	25 (Physical Mixture)	26.6

nated with zinc chloride.

Zinc bromide shows the same effect as zinc chloride. Aluminum chloride, another Lewis acid, shows a similar effect, but comparison is difficult because of the greater volatility of aluminum chloride. Stannous chloride, a good catalyst for coal hydrogenation but chemically different from zinc chloride, shows the same effect as zinc chloride. A coal sample with 5% $SnCl_2$ impregnated from solution shows a weight loss of 32.9%. With 12% $SnCl_2$, the weight loss is reduced to 27.2%, and with 20% $SnCl_2$, the weight loss is only 21.7%.

Kenney and Takahashi[5] studied the catalytic dehydrohalogenation of alkyl halides by molten zinc chloride. They suggested that an ionic complex is formed by transfer of the halide to the $ZnCl_2$ to form a carbonium ion and $ZnCl_3^-$. Alkyl halides decreased the activity, presumably by forming $ZnCl_3^-$ and $ZnCl_4^=$. Zielke et al[2] postulated the active species in hydrocracking of polynuclear aromatic molecules to be $H^+(ZnCl_3^-)$ or $H^+(ZnCl_2OH^-)$ formed by the reaction of $ZnCl_2$ with HCl or with H_2O. The possible role of $ZnCl_3^-$ in reducing the volatility of coal was investigated by impregnating sodium chloride and zinc chloride on the coal. The zinc chloride was held at 12% by weight of the coal and the sodium chloride was 10, 20, 30 and 50% by weight of the zinc chloride. There was no difference in the weight loss of coal in these samples and that of coal with 12% zinc chloride. When sodium chloride alone is impregnated on coal, the weight loss is the same as for pure coal.

Coal and zinc chloride were physically mixed rather than impregnating the zinc chloride onto the coal. The thermal analysis results are shown in Table I. The results are similar to those for impregnated samples although the physical mixture is slightly less effective in reducing volatility at higher percentages.

Analysis of the gaseous pyrolysis product was performed by gas chromatography. Methane is the major gaseous product over the entire temperature range. Ethane, propane, and butanes are produced in significant quantities below 500°C. In comparing the gaseous products from coal with those from zinc chloride-impregnated coal, very little difference is noted. The total amount of gases is decreased in the presence of zinc chloride but the composition of the gas is unchanged.

Zinc chloride is a relatively strong Lewis acid. Stannous chloride is only a moderately active Lewis acid. Wood[6] finds that Lewis acids such as $ZnCl_2$, $ZnBr_2$, ZnI_2 are good catalysts for coal hydrogenation in a short-resident time reactor. Ferric chloride, which is a Lewis Acid, did not show appreciable activity. Stannous chloride was comparable to zinc chloride. Zinc sulfate and other metal chlorides such as $CuCl_2$, $CrCl_3$ and $CdCl_2$ show little catalytic activity.

The mechanism of coal hydrogenation by zinc chloride is not clear. It is not certain that zinc chloride and stannous chloride function by the same mechanism. The decreased volatility of coal, caused by impregnating catalyst on the surface, appears to be a chemical effect rather than a physical effect. Physical entrapment of reactive fragments from pyrolysis does not appear to be the major factor, since physical mixtures behave very nearly like impregnated samples and because impregnated sodium chloride is uneffective. Weller et al[7] proposed a mechanism for coal hydrogenation in which tin acts to stabilize reactive fragments with the addition of hydrogen. The zinc chloride also appears to stabilize reactive fragments in this study. In the absence of hydrogen, these reactive fragments polymerize to produce non-volatile products, thus reducing the volatile content of the coal.

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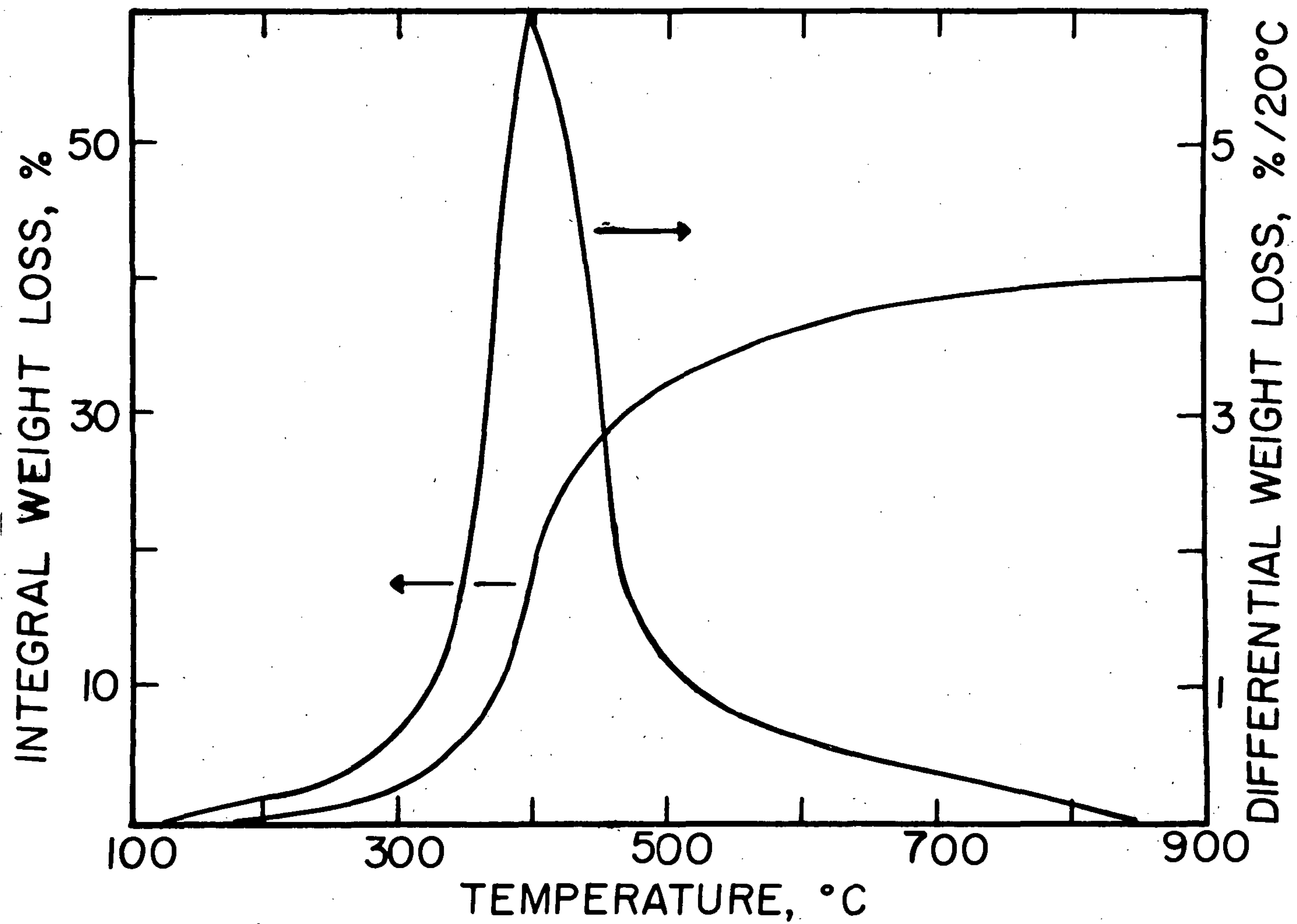

FIGURE 1. THERMOGRAVIMETRIC ANALYSIS OF COAL

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